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Synthesis, characterization, electrochemical and CO_2 sensing properties of novel mono and ball-type phthalocyanines with four phenolphthalein units

Selçuk Altun[a], Ahmet Altındal[b], A. Rıza Özkaya[a], Mustafa Bulut[a], Özer Bekaroğlu[c,*]

[a] Department of Chemistry, Marmara University, 34722 Göztepe-İstanbul, Turkey
[b] Department of Physics, Marmara University, 34722 Göztepe-İstanbul, Turkey
[c] Department of Chemistry, Technical University of İstanbul, Maslak-İstanbul, Turkey

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ABSTRACT

The novel mono metallo [Zn(II) **4** and Co(II) **5**] and ball-type or cofacial bis-metallo [Zn(II) **6** and Co(II) **7**] phthalocyanines have been synthesized from **3**, which can be obtained by the reaction of 4-nitrophthalonitrile **1** with 3,3-bis(4-hydroxy-phenyl)isobenzofuran-1(3*H*)-one **2** (phenolphthalein). The phthalocyanines have been characterized by elemental analysis, UV–vis, IR, ^{1}H NMR, and mass spectroscopy. The redox behavior of the complexes was investigated by cyclic voltammetry and controlled-potential coulometry. The electrochemical measurements suggested the formation of mixed-valent species during the redox processes of bis-metallophthalocyanines **6** and **7**, as a result of the intramolecular interactions between two cofacial Pc units. The effect of temperature on the CO_2 sensing properties of a spin-coated thin film of **7** was also investigated.

1. Introduction

Phenolphthalein (PP) is a well-known acid–base indicator. PP exists as the colorless lactone form (H_2PP) at pH values lower than 8. As the pH rises from 8 to 10, it is generally accepted that the dianion form (PP^{2-}) is responsible for the familiar red-pink color.[1] On the other hand, phthalocyanines (Pcs) and their derivatives display interesting electrical and electrochemical properties which are important for applications in chemical sensors, liquid crystals, catalysis, nonlinear optics, optical data storage, and nanotechnology.[2–4] Recently, attention has been attracted to ball-type or cofacial bis-phthalocyanines containing two metal centers, due to their interesting properties. Various ball-type phthalocyanines were synthesized for the first time by the group of Zefirov and co-workers.[5,6] Later, various ball-type Pcs were synthesized and investigated in terms of their electrical, electrochemical and nonlinear optical properties, by our group.[7–14] These compounds were prepared via a one-step reaction. In this study, the cofacial bis-metallo phthalocyanines **6** and **7** have been synthesized in two steps, for the first time (Scheme 1). Compounds **4** and **5** were obtained by heating **3** without solvent, and then compounds **6** and **7** were synthesized by reaction of **4** and **5** with the respective metal salts in DMF.

As is well known, carbon dioxide contributes to the green-house effect and, possibly, respiratory organ diseases. Therefore, the detection and the control of CO_2 concentration are extremely important. Accordingly, much effort has been devoted to the development of sensing methods for CO_2 gas.

Elemental analysis, IR, ^{1}H NMR (300 MHz), mass, and UV–vis spectra confirmed the proposed structures of the compounds **3**–**7**. The IR spectra were obtained from KBr discs. The C≡N stretches appeared at 2229–2231 cm^{-1} as single peaks in the spectra of **4** and **5**. The spectra of compounds **3**–**7** showed Ar–O–Ar peaks at 1220–1285 cm^{-1}, C=C peaks at 1560–1655 cm^{-1}, C=O peaks at 1760–1780 cm^{-1}, C=N peaks at 1670–1720 cm^{-1}, and aromatic CH peaks at 3060–3080 cm^{-1}. The ^{1}H NMR spectra also correlated well with the structures of the synthesized compounds. The UV–vis spectra of **4**, **5**, **6** and **7** in tetrahydrofuran (THF) showed characteristic Q band absorptions around 670 nm, which were attributed to the $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in the UV region at 300–350 nm were due to transitions from the deeper π levels to the LUMO. The molecular ion peaks of **4**, **5**, **6** and **7** were observed at 2347, 2341, 2413, and 2400 Da, respectively. Additional peaks for H_2O, $2H_2O$, and $3H_2O$ adducts were also assigned.

The response and recovery properties of a spin-coated film of **7** at room temperature under a CO_2 atmosphere (10,000 ppm) are shown in Figure 1. Once CO_2 was introduced into the test cell, the conductivity of the sensor increased during the initial doping stage for a few minutes and then the rate of increase slowed down. This could be explained in terms of the formation of acceptor states which lie below the Fermi level during the initial stage of

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* Corresponding author. Tel.: +90 216 359 01 30; fax: +90 216 386 08 24.
E-mail address: obek@itu.edu.tr (Özer Bekaroğlu).

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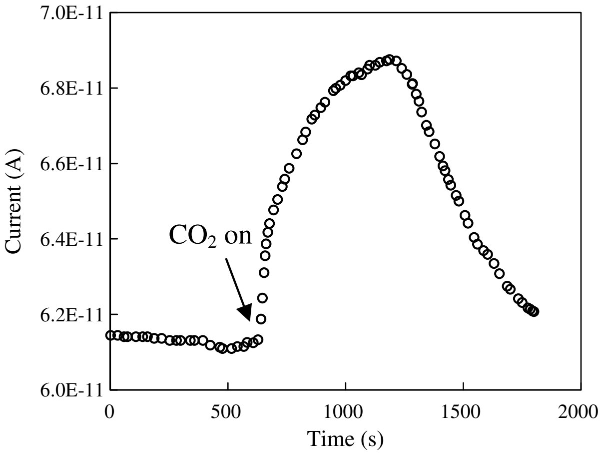


Figure 1. The response characteristic of a spin-coated thin film of **7** to 10,000 ppm CO_2 gas at room temperature.

adsorption.[15] From impedance measurements, semicircular-shaped curves, the diameter of which decreased with increased CO_2 concentration, were obtained. These results indicate a charge transfer interaction between the phthalocyanine rings and the target molecules.

The electrochemical properties of complexes **4**–**7** were investigated by cyclic voltammetry (CV) and controlled-potential coulometry (CPC) in dimethylsulfoxide/tetra-butylammonium perchlorate (DMSO/TBAP). The voltammetric data for the complexes are collected in Table 1. Cyclic voltammograms of mono ZnPc **4** and ball-type ZnPc **6** are shown in Figure 2. The occurrence of stepwise one-electron processes for cofacial bis-metallophthalocyanines **6** and **7** involving two Pc rings and two metal centers, and the comparison of their half-peak potentials with those of monophthalocyanines **4** and **5** imply that binding of the two Pc rings rigidly on both sides with four linking arms in **6** and **7** leads to remarkable intramolecular coupling, and hence splitting of the classical monophthalocyanine redox processes of **4** and **5**. This type of redox behavior was observed previously for similar cofacial bis-metallophthalocyanines,[11,12,16,17] and is consistent with the rigid structure of these complexes. In situ spectroelectrochemical studies of the complexes are continuing with the aim of providing additional support for the assignment of redox processes of the complexes, and the results will be discussed in detail in a further report.

Table 1
Electrochemical data for **4-7** in DMSO/TBAP

Complex	Redox process	$E_{1/2}$(V vs SCE)[a]	n[c]
4	1st oxidation	0.68	1
	1st reduction	−0.76	1
	2nd reduction	−1.18	1
	3rd reduction	−1.54	4
5	1st oxidation	0.43	1
	1st reduction	−0.29	1
	2nd reduction	−1.00	1
	3rd reduction	−1.47	4
6	1st oxidation	0.85	1
	1st reduction	−0.39	1
	2nd reduction	−0.64	1
	3rd reduction	−1.18	1
	4th reduction	−1.45[b]	–
7	1st reduction	−0.19	1
	2nd reduction	−0.62	1
	3rd reduction	−1.14	1
	4th reduction	−1.39	–

[a] $E_{1/2}$ values were measured by cyclic voltammetry [$E_{1/2} = (E_{pa} + E_{pc})/2$].

[b] Cathodic peak potential.

[c] The number of electrons transferred per molecule was determined from controlled-potential coulometric measurements. The values for the last reduction processes of **6** and **7** could not be determined due to the ill-defined redox couples detected at high negative potentials.

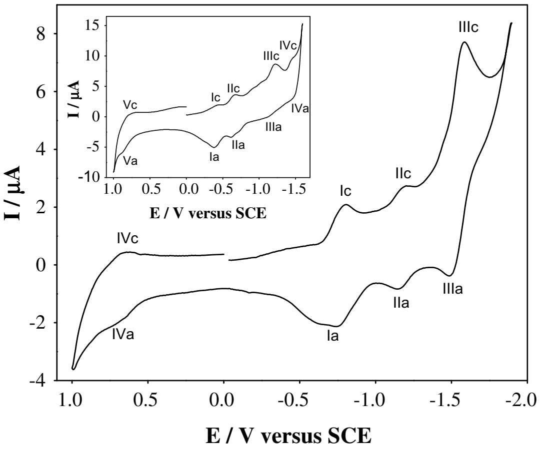
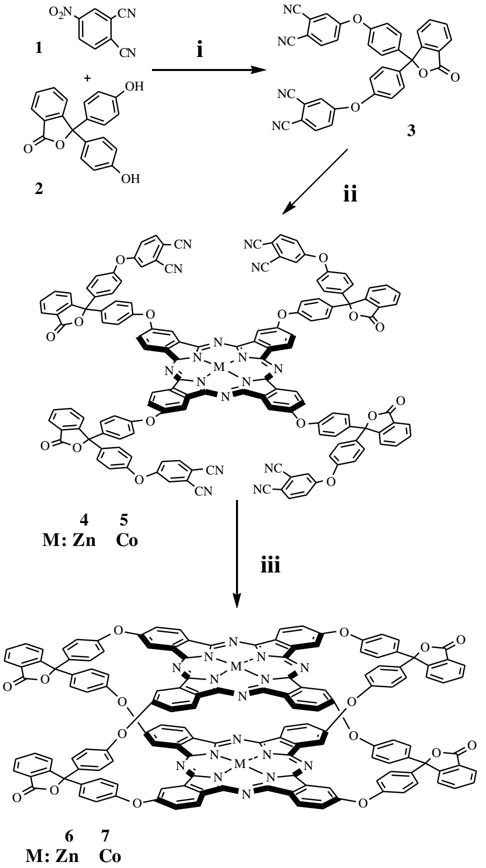


Figure 2. Cyclic voltammograms of **4** and **6** (inset) at 0.050 V s^{-1} in DMSO/TBAP.



Scheme 1. Synthesis of compounds **4, 5, 6**, and **7**. Reagents and conditions: (i) K_2CO_3, N_2, DMSO, rt, 24 h; (ii) $Zn(OAc)_2{\cdot}2H_2O$ or $Co(OAc)_2{\cdot}4H_2O$, 320 °C, 5 min; (iii) $Zn(OAc)_2{\cdot}2H_2O$ or $Co(OAc)_2{\cdot}4H_2O$, N_2, DMF, reflux temperature, 24 h.

2. Experimental

The starting material **1** was synthesized by using the literature method.[18] Compound **2** was commercially available.

For voltammetric experiments, the working electrode was a Pt plate with a surface area of 0.10 cm^2. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. Anhydrous N_2 was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. For CPC studies, a Pt gauze working electrode (10.5 cm^2 surface area), a Pt wire counter electrode separated by a glass bridge, and a SCE as reference electrode were used.

The electrical conductivity and impedance spectra of the spin-coated film under various gas concentrations were measured at different temperatures. In a typical run, pure nitrogen was first introduced into the test chamber at a flow rate of 100 mL/min for at least 30 min. Then, well defined concentrations of CO_2 gas were prepared by mixing the reference gas with the target gas. The concentration of the target gas was varied by using a MKS Instrument mass flow controller.

2.1. Synthesis of [4,4′-(4,4′-(3-oxo-1,3-dihydroisobenzo furan-1,1-diyl) bis(4,1-phenylene)bis(oxy))] diphthalo nitrile 3

Compound **3** was obtained by a nitro displacement reaction according to the literature.[19] A mixture of 4-nitro-1,2-dicyanobenzene **1** (0.657 g, 3.8 mmol) and 3,3-bis(4-hydroxy-phenyl)isobenzofuran-1(3*H*)-one, **2** (0.604 g, 1.9 mmol) in 20 mL of dry DMSO was stirred at room temperature under N_2. K_2CO_3 (0.828 g, 6 mmol) was added to the mixture for over a period of 2 h. After stirring the reaction mixture for a further 24 h, the undissolved salt was removed by filtration. The reaction mixture was poured into water (100 mL) and stirred. The resulting precipitate was filtered and washed with water. The residue was chromatographed over silica gel and eluted with CH_2Cl_2. Yield; 1.14 g (96%). This compound is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, acetone, acetonitrile, and acetic acid. Mp: 242 °C. IR (KBr pellet) $\nu_{\max/\text{cm}^{-1}}$: 841, 962, 1086, 1174, 1251, 1282, 1421, 1487, 1566, 1591, 1768, 2235, 3078. Anal. Calcd for $C_{36}H_{18}N_4O_4$: C, 75.78; H, 3.18; N, 9.82. Found: C, 75.65; H, 3.22; N, 9.78. ^{1}H NMR (DMSO-d_6) δ 8.08 (dd, *J* = 8.8 Hz, *J* = 0.6 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.3 Hz, 1H), 7.86 (d, *J* = 0.6 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 2H), 7.45 (d,*J* = 6.0 Hz, 4H), 7.41 (dd, *J* = 7.2 Hz, *J* = 0.8 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 4H) ppm.

2.2. Synthesis of [2,10,16,24-tetrakis(phenolphthaleinyl) phthalocyaninato zinc(II)] 4 and [2,10,16,24-tetrakis (phenolphthaleinyl) phthalocyaninato cobalt(II)] 5

Compound **3** (0.2 g, 0.35 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (0.100 g, 2.4 mmol) were powdered in a quartz crucible and heated in a sealed glass tube for 5 min under a dry N_2 atmosphere at 320 °C. After cooling to room temperature, a green-colored reaction product was obtained. DMF (5 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding acetic acid. The precipitate was filtered, washed with hot acetic acid and then with hot methanol in order to eliminate unreacted starting materials, and finally dried in vacuo. The residue was fractionated on a silica gel column eluting with chloroform–THF. Yield of **4**: 48 mg (23%) Compound **4** is slightly soluble in CH_2Cl_2 and $CHCl_3$, and is soluble in THF, DMF, and DMSO. Mp >350 °C. IR (KBr pellet) $\nu_{\max/\text{cm}^{-1}}$: 838, 941, 1085, 1174, 1234, 1392, 1469, 1498, 1595, 1766, 2231, 3058. Anal. Calcd for $C_{144}H_{72}N_{16}O_{16}Zn$: C, 73.67; H, 3.09; N, 9.55. Found: C, 73.55; H, 3.02; N, 9.68. UV–vis (THF), nm (log ε, M^{-1} cm^{-1}): 350 (4.749), 611 (4.426), 674 (5.045), ^{1}H NMR (DMSO-d_6) δ, ppm: 7.1–8.1 (m, 72H, arom-CH), (MALDI-TOF): *m/z* 2347 (M$^+$).

Complex **5** was synthesized using a similar procedure to that as described above for **4**. Yield of **5**: 62 mg (30%). Compound **5** is slightly soluble in DCM and $CHCl_3$, and soluble in THF, DMF, and DMSO. Mp >350 °C. IR (KBr pellet) $\nu_{\max/\text{cm}^{-1}}$: 756, 837, 1099, 1168, 1238, 1411, 1469, 1504, 1597, 1770, 2230, 2850, 2916, 3074. Anal. Calcd for $C_{144}H_{72}N_{16}O_{16}Co$: C, 73.88; H, 3.10; N, 9.57. Found: C, 73.93; H, 3.16; N, 9.49. UV–vis (THF), nm (log ε, M^{-1} cm^{-1}): 331 (5.019), 603 (4.643), 668 (5.191), (MALDI-TOF): *m/z* 2341 (M$^+$).

2.3. Synthesis of [2′,10′,16′,24′-(tetrakis-phenolphthaleinyl)-bis-phthalocyaninatodi-zinc(II)] 6 and [2′,10′,16′,24′-(tetrakis-phenolphthaleinyl)-bis-phthalocyaninatodi-cobalt(II)] 7

Compound **4** (0.02 g, 0.0085 mmol) and excess $Zn(OAc)_2.2H_2O$ were dissolved in 6 mL of DMF. The reaction mixture was refluxed under a dry N_2 atmosphere for 24 h. The product was precipitated by adding acetic acid. The precipitate was washed several times at first with hot acetic acid and then with hot methanol, and finally dried in vacuo. Yield of **6**: 18 mg (90%).

Compound **6** is soluble in THF, DMF, and DMSO. Mp >350 °C. IR (KBr pellet) $\nu_{\max/\text{cm}^{-1}}$: 748, 841, 945, 1045, 1169, 1234, 1361, 1396, 1473, 1504, 1600, 1720, 1770, 2850, 2924, 3066. Anal. Calcd for $C_{144}H_{72}N_{16}O_{16}Zn_2$: C, 71.68; H, 3.01; N, 9.29. Found: C, 71.54; H, 3.0; N, 9.17. UV–vis (THF), nm (log ε, M^{-1} cm^{-1}): 351 (4.878), 609 (4.544), 674 (5.236), ^{1}H NMR (DMSO-d_6) δ, ppm: 7.27–8.1 (m, 72H, arom-CH), MS (MALDI-TOF): *m/z* 2413 (M$^+$).

Complex **7** was synthesized in a similar manner to that described above for **6**, using cobalt acetate. Yield of **7**: 19 mg (95%).

Compound **7** is soluble in THF, DMF and DMSO. Mp >350 °C. IR (KBr pellet) $\nu_{\max/\text{cm}^{-1}}$: 752, 841, 929, 957, 1014, 1057, 1099, 1165, 1234, 1381, 1408, 1470, 1504, 1601, 1713, 1770, 2858, 2912, 3066. Anal. Calcd for $C_{144}H_{72}N_{16}O_{16}Co_2$: C, 72.06; H, 3.02; N, 9.34. Found: C, 71.92; H, 3.14; N, 9.52. UV–vis (THF), nm (log ε, M^{-1} cm^{-1}): 324 (4.734), 602 (4.568), 669 (4.929), (MALDI-TOF): *m/z* 2400 (M$^+$).

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